

## Insulating gap in FeO: Correlations and covalency

I. I. Mazin

*Max-Planck-Institut für Festkörperforschung, Stuttgart D-70569, Germany  
and Geophysical Laboratory and Center for High-Pressure Research, Carnegie Institution of Washington,  
5251 Broad Branch Rd. N.W., Washington, D.C. 20005-1305*

V. I. Anisimov

*Max-Planck-Institut für Festkörperforschung, Stuttgart D-70569, Germany  
and Institute for Metal Physics, Ekaterinburg, Russia*

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We report calculations of the electronic structure of FeO in the local-density approximation (LDA) and LDA+ $U$  approximation with and without rhombohedral distortion. In both cases LDA renders an antiferromagnetic metal, and LDA+ $U$  opens a Hubbard gap. However, the character of the gap is qualitatively different in the two structures, and the difference can be traced down to the underlying LDA band structure. An analysis of the calculations gives insight into the origin of the insulating gap in 3d monoxides, and into the role of the  $\mathbf{k}$  dependency of  $U$ , missing in the contemporary LDA+ $U$  method. [S0163-1829(97)10416-7]

It is a well-known fact that conventional band-structure calculations incorrectly give a metallic ground state for the intermediate 3d transition-metal monoxides CoO and FeO. Before the high- $T_c$  cuprates entered the scene, this had been often considered as the most notable failure of the local density approximation (LDA). In the past decade a number of extensions of density-functional theory (DFT) were suggested, which, in different manners, led to insulating ground states for these compounds. Most successful were various flavors of the self-interaction corrected LDA,<sup>1</sup> LDA+ $U$ ,<sup>2</sup> and the orbital polarization correction in a crystal-field basis.<sup>3</sup> Interestingly, apart from the gap itself, the LDA appears to do as good a job as, and sometimes a better job than, these sophisticated extensions, especially when gradient corrections to the LDA are taken into account. Structural properties are reproduced very well, including rhombohedral distortion in FeO,<sup>4</sup> and its increase with pressure.<sup>5</sup> Moreover, photoemission renders the bands more similar to LDA bands than to those in other calculational schemes (except for the narrow range near the gap).<sup>7</sup> The magnitude of the magnetic moment, which is often believed to be the first indication of a LDA failure, is nearly exact for the spin moment in CoO ( $2.4\mu_B$ ) and FeO ( $3.5\mu_B$ , assuming no orbital moment). Conversely, the gap-improving calculation tends to overestimate the Fe moment, especially when the orbital moment is included (i.e., there is a tendency<sup>3</sup> to underestimate the quenching of the orbital moment). It seems, then, that the main problem in the LDA is purely spectroscopical (quite in the spirit of the DFT), namely, the nonexistence of the gap. It is worth noting that an important common feature of the LDA and the corrected schemes mentioned above is the substantial width of the metal  $d$  bands (for instance, in the LDA, the width of the Fe  $t_{2g}$  band at normal pressure is about 1.4 eV). This should be contrasted with the popular analysis of the electronic structure of 3d oxides in terms of separate levels of a width less than Jahn-Teller energy and spin-orbital coupling.<sup>6</sup>

The fact that LDA gaps are too small is well understood. Mathematically it appears as the density-derivative discontinuity of the Kohn-Sham potential in the DFT. The physics of

this may be different, but for transition-metal oxides (NiO, MnO) it is usually associated with Mott-Hubbard repulsion.<sup>3</sup> In view of this, it has always been much more disturbing to have, wrongly, a metallic behavior in the LDA calculation than just to have a wrong gap. As formulated by Norman,<sup>3</sup> “one would like to obtain a gap at the level of a density-functional calculation (no matter how small) so as to define the Mott-Hubbard correction in an unambiguous fashion.” Moreover, even in a case when the LDA does not give a gap, but gives a reasonable band structure except for the immediate vicinity of the Fermi level, and correctly describes delicate features of the ground state, such as magnetoelastic interactions, it is desirable to have a correction scheme which does not destroy the LDA bands completely, but rather corrects them in a systematic manner. Unfortunately none of the schemes above acts in such a way. In this paper we shall analyze the results of the rotationally invariant LDA+ $U$  (Ref. 9) calculations for FeO in more detail than is usually done, and compare them with the standard LDA calculations, paying particular attention to the LDA+ $U$  gap opening in cubic and rhombohedral structures. We will see that the ground state in the LDA+ $U$  approach is intimately related with the underlying LDA band structure, although LDA+ $U$  cannot fully account for the band hybridization effects, which seem to be quite important here. We will argue that none of the existing “corrected LDA” schemes (nor the straight LDA) correctly describes the ground state in FeO and similar compounds. On the other hand, nonlocal schemes similar to the  $GW$  approximation may provide a qualitatively correct description. It is worth noting that none of the existing “extended-LDA” calculations has taken into account such an important factor as the distortion from the ideal cubic NaCl-type structure, which is associated in 3d monoxides with the onset of magnetic ordering.

The electronic structure of an isolated Fe<sup>2+</sup> ion in a cubic field in the high-spin state is described by the following scheme:<sup>8</sup> The spin-up  $d$  states are all filled, and are separated from the spin-down states by the exchange splitting  $E_{ex}$ . The partially occupied spin-down states are split by the crystal field, so that  $\epsilon(e_g) - \epsilon(t_{2g}) = \Delta \ll E_{ex}$ . There is one electron

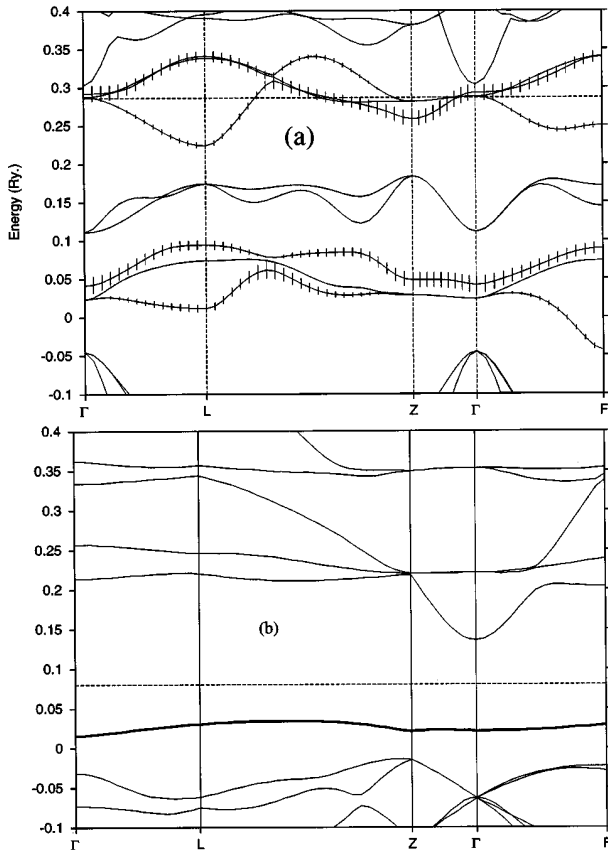


FIG. 1. (a) LDA band structure without a rhombohedral distortion. The bars show the relative  $A_{1g}$  character of the corresponding states (it is not possible to single out a unique band with this character). (b) LDA+ $U$  bands for the same crystal structure. The (nearly pure)  $A_{1g}$  band is bold. The parabolic band just above the Fermi level (which is shown by dashed lines in all figures), with the bottom at the  $\Gamma$  point, is predominantly Fe( $s$ ).

in the triply degenerate  $t_{2g\downarrow}$  state. Antiferromagnetic FeO has alternating close-packed (111) planes of Fe ions with opposite spins, lowering the symmetry to a rhombohedral one. In the rhombohedral field, there is one combination of the  $t_{2g}$  states, namely,  $A_{1g} = (xy + yz + zx)/\sqrt{3}$ , which can also be written as  $3Z^2 - r^2$ , where  $Z$  is parallel to  $[111]$  (here and below we shall use lower case symbols for the cubic nomenclature and upper case symbols for the rhombohedral nomenclature). The four other states have the same symmetry  $E_g$ , but when the deviation from the cubic symmetry is small one can speak about the upper two levels  $E_g''$ , and the lower two levels  $E_g'$ , which are close to  $A_{1g}$ , also originate from cubic  $t_{2g}$  states, and are separated from  $E_g''$  by approximately  $\Delta$ . In the LDA calculation, when the lattice symmetry is still cubic, although the magnetic ordering is rhombohedral, the splitting between  $E_g'$  and  $A_{1g}$  is small, much smaller than their bandwidths, so that they merge into one band (corresponding to the cubic  $t_{2g}$  band), which is necessarily metallic. Although the magnetism in this system appears to be due to the superexchange and is determined by the O-Fe  $pd$  interaction, the width of the  $t_{2g}$  band is mainly due to the Fe-Fe  $dd\sigma$  overlap. Fe-O hopping for this band is mainly  $pd\pi$  and weak. The situation in CoO with two  $t_{2g}$  electrons is very similar.

There were several successful attempts to obtain an insulating state in FeO.<sup>1-3</sup> They all give an insulating gap in fair agreement with the experiment, but all for different reasons.

TABLE I. Orbitals and their occupations without rhombohedral distortion, for  $U=5.1$ . The character of the orbitals is  $2 \times E_g''$ ,  $2 \times E_g'$ , and  $A_{1g}$ .

Occupation	$xy$	$yz$	$3z^2 - 1$	$xz$	$x^2 - y^2$
0.04	-0.10	-0.10	0.00	0.68	0.72
0.04	0.72	0.68	0.00	0.10	0.10
0.10	0.53	-0.57	0.00	-0.46	0.43
0.10	-0.43	0.46	0.00	-0.57	0.53
0.90	0.00	0.00	1.00	0.00	0.00

SIC calculations<sup>1</sup> favor  $d$  bands in pure orbital states, that is, undermining the role of crystal field and quenching of orbital moment. The effect on the occupied  $d$  states is thus extremely strong (of the order of 1 Ry), and all four oxides come out as pure charge-transfer insulators. This is in contradiction with the general experimental indication that the character of the band gap changes from predominantly Mott-Hubbard to predominantly charge transfer when going from MnO to NiO. A large orbital moment is obtained for FeO, in contradiction with the experiment (an argument is usually made that the experimental number may be incorrect because of poor sample quality). In fact, self-interaction correction was initially proposed as a remedy for the LDA in the direction of the exact, self-interaction-free DFT. It is hard to imagine, however, that the exact DFT with its orbital-independent one-electron potential can unquench the orbital moment.

The orbital-corrected functional used by Norman<sup>3</sup> has a similar problem. The correct many-body solution for an isolated ion with an unfilled  $t_{2g}$  shell in a cubic field<sup>8</sup> includes an energy contribution proportional to the total angular momentum. This term, however, does not favor a specific direction of the momentum. The only interaction which does unquench the orbital momentum is a weak spin-orbit one. Norman's correction has the same functional form as the exact quantum-chemical expression,<sup>8</sup> but substitutes the total momentum with its projection on the quantization axis. This orbital moment projection-dependent term acts in a way similar to the spin-orbit coupling, but with a much larger magnitude (of the order of exchange splitting  $J$ ). Thus in FeO the occupied spin-down  $d$  band is too close to a pure  $m=1$  state, that is,  $xz + iy_z$ .

LDA+ $U$  is equally successful in predicting a band gap (Fig. 1), but forms a completely different insulating state. There is no mechanism for unquenching the orbital moment, apart from the spin-orbit coupling, neglected in Ref. 2 and other LDA+ $U$  calculations. LDA+ $U$  starts from the straight LDA bands, where the  $t_{1g}$  bands are strongly mixed, the  $A_{1g}$  orbital being slightly more occupied than each of the two  $E_g'$  orbitals. In a rotationally invariant form,<sup>9</sup> LDA+ $U$  tends to apply the positive- $U$  correction to less occupied  $E_g'$  orbitals, making them less and less filled (the potential  $U$  correction for the more filled  $A_{1g}$  orbital is negative), and eventually splits off the  $A_{1g}$  band, forming a gap between it and the  $E_g'$  bands. Sufficiently large  $U$  (we used the empirical value of  $U=5.1$  eV;<sup>10</sup> constraint LDA calculations<sup>11</sup> yield  $U=6.8$  eV) pushes the occupied  $A_{1g}$  band down close to, and for  $U=6.8$  eV right into, the

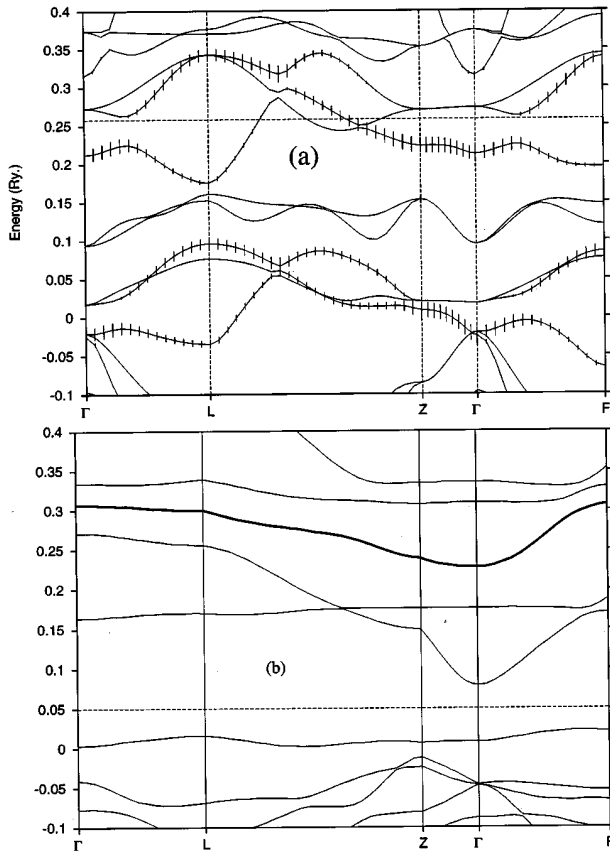


FIG. 2. The same as Fig. 1, but with a rhombohedral distortion of 6%.

O( $p$ ) band manifold, and the unoccupied  $E'_g$  bands up above the bottom of the Fe( $s$ ) band. This seems to be in qualitative agreement with the photoemission experiments, which show the top of the valence band to be of the mixed O $2p$ -Fe $3d$  character,<sup>12</sup> and with the optical experiments, which indicate a weak absorption between 0.5 and 2.0 eV, assigned to the ( $pd$ )- $s$  transitions, and a strong absorption edge at 2.4 eV due to transitions into the Fe( $d$ ) band.<sup>13</sup> In our calculations, the minimal gap opens between the O( $p$ )-Fe( $d$ ) band and the Fe( $s$ ) band at 1.3 eV, and transitions into the Fe( $d$ ) band start at 2.2 eV.

LDA and the LDA+ $U$  bands refer to the cubic FeO [here and below we show results of the atomic-sphere-approximation linear muffin-tin orbital<sup>15</sup> (LMTO) calculations with a unit-cell volume  $256 \text{ bohr}^3/\text{FeO}$ , close to the LDA equilibrium volume<sup>5</sup>]. Since only one orbital,  $A_{1g}$ , is occupied (see Table I), there is no orbital moment. One can expect that including weak (a few m Ry) spin-orbit coupling will create a small orbital moment, but hardly one comparable with the spin magnetization. The way the gap opens in LDA+ $U$  in the cubic structure is very ‘‘LDA-like.’’ The only way to open a gap in an effective one-electron approximation is to split the  $t_{2g}$  band by rhombohedral symmetry, and to occupy the  $A_{1g}$  orbital for FeO and the two  $E'_g$  orbitals in CoO. In fact, this is exactly what happened in the LDA calculations of Dufek, Blaha, and Schwarz,<sup>14</sup> who used an exotic LDA functional, which gave poor total energies but did open gaps in both compounds.

Overall this seems to be a physically satisfactory description of the gap opening. However, this is not as straightforward as one may think. To show the problem, let us compare

TABLE II. Orbitals and their occupations without rhombohedral distortion, for  $U=0$ . The coordinate system corresponds to the rhombohedral symmetry: the  $z$  axis is perpendicular to the ferromagnetic Fe planes, and the  $y$  axis points toward the nearest-neighbor Fe plane with like spin. The character of the orbitals is, in the order of the table,  $2 \times E'_g$ ,  $2 \times E''_g$ , and  $A_{1g}$ .

Occupation	$xy$	$yz$	$3z^2-1$	$xz$	$x^2-y^2$
0.17	-0.03	0.03	0.00	-0.65	0.76
0.17	0.75	-0.66	0.00	-0.03	0.03
0.31	0.60	0.69	0.00	0.30	0.26
0.33	-0.26	-0.30	0.00	0.69	0.60
0.39	0.00	0.00	1.00	0.00	0.00

the calculations in the cubic structure with those in the rhombohedrally distorted structure (Fig. 2; we used the LDA equilibrium distortion, calculated in Ref. 5; experimental distortion is smaller, but increases with the pressure). To understand the result, one should keep in mind that dispersion of the  $t_{2g}$  bands is mainly due to direct  $dd\sigma$  hopping between like spins, which can be easily verified in the LMTO tight-binding (TB) method by removing oxygen orbitals from the basis set, or by looking directly on the corresponding elements of the LMTO-TB Hamiltonian. We observe that the distortion increases the  $t_{2g}$  bandwidth (due to decreased distance between the like-spin ions), but mainly at the expense of the  $E'_g$ -like bands. The dispersion of the  $A_{1g}$  band decreases instead, thus leading to a decreased occupancy of the  $A_{1g}$ -like state (because the whole  $t_{2g}$  manifold is less than half-filled). One can see this by comparing the occupancy matrices in the cubic (Table II) and in the distorted (Table III) structure on the first iteration, i.e., before the effect of  $U$ . While in the cubic structure the  $A_{1g}$  state was the mostly occupied one (with the two  $E'_g$  states close next), in the distorted structure the  $E'_g$  states are twice as occupied as the  $A_{1g}$  one.

Our rotationally invariant LDA+ $U$  (Ref. 9) code applies  $U$  corrections to states which are arbitrary linear combinations of the  $d$  orbitals with various  $m$ . The coefficients of this combination are chosen self-consistently so that they optimize the total energy including the Coulomb one. In the case of the rhombohedrally distorted FeO it is unfavorable to occupy the  $A_{1g}$  orbital, not because of the Hubbard energy, but because of the one-electron energy: the same reason why the LDA deoccupied this orbital after distortion. How does LDA+ $U$  handle this situation during the self-consistency cycle? It is left with the only possibility to make a linear

TABLE III. Orbitals and their occupations with 6% rhombohedral distortion, for  $U=0$ . The characters are  $2 \times E'_g$ ,  $A_{1g}$ , and  $2 \times E''_g$ .

Occupation	$xy$	$yz$	$3z^2-1$	$xz$	$x^2-y^2$
0.17	-0.55	0.84	0.00	-0.02	0.01
0.17	-0.01	0.02	0.00	0.83	-0.56
0.19	0.00	0.00	1.0	0.00	0.00
0.38	0.84	0.55	0.00	0.00	-0.00
0.39	-0.01	-0.01	0.01	0.56	0.83

combination of the  $E'_g$  orbitals with a possible admixture of the  $E''_g$  states, as much as the crystal field allows, to make it a separate band and to open a gap between this band and the rest of the spin-minority  $d$  bands (Table IV).

One may feel it unphysical that the method converges to qualitatively different ground states with and without distortion. Probably the correct solution should be intermediate between the two LDA+ $U$  stationary points, a completely full and a completely empty  $A_{1g}$  state. Indeed, a closer look at the LDA band structure of Fig. 2(a) shows that along the whole  $\Gamma$ -Z (111) direction the  $A_{1g}$  band lies entirely below the Fermi level. In the other parts of the Brillouin zone (points  $L$  and  $F$ ) it is completely above the Fermi level. Thus a  $U$  matrix acting on an unoccupied  $A_{1g}$  orbital has to overcome the natural LDA tendency along the  $\Gamma$ -Z line, although it is in accord with the LDA tendencies in the rest of the zone.

Now one can see that the problem with the LDA+ $U$  is that the  $U$  matrix is  $\mathbf{k}$  independent: it is a matrix in the orbital space,  $U_{mm'}$ ,  $-2 \leq m \leq 2$ , and this matrix does not depend on whether the particular  $d$  electron is in a bonding or antibonding interaction with the neighboring sites. While this may be a good approximation for extremely localized electrons, in such materials as FeO one cannot neglect the fact that  $d$  orbitals extend into neighboring sites. In the LMTO scheme the tails of each orbital, penetrating into an atomic sphere of a neighboring site, are reexpanded and, depending on the LMTO flavor ("representation"), may or may not appear in the density matrix at the same site as its head.<sup>16</sup> In the conventional LDA+ $U$  scheme, as well as in all other correction schemes discussed above, only the heads of the LMTO's are subject to a correction. On the other hand, a more realistic correction would also apply to that part of a  $d$  orbital that penetrates into the neighboring spheres. In other words, a physically sound implementing of such a correction should be essentially nonlocal. Hartree-Fock-like schemes, similar to the  $GW$  approximation,<sup>17</sup> should be able to reproduce the correct physics. For instance, one can expect that the occupied band, which appears to be purely  $A_{1g}$  in the cubic case and purely  $E'_g$  in the distorted case, would have a mixed character, being more  $A_{1g}$ -like close to the  $\Gamma$ -Z line. Correspondingly, the effective  $U$  matrix would be different when applied at different  $\mathbf{k}$  points. Another interesting alternative is offered by non-Kohn-Sham versions

TABLE IV. Orbitals and their occupations with 6% rhombohedral distortion, for  $U=5.1$ . The characters are  $A_{1g}$ ,  $E''_g$ ,  $2 \times E'_g$ ,  $A_{1g}$ , and  $E''_g$ .

Occupation	$xy$	$yz$	$3z^2-1$	$xz$	$x^2-y^2$
0.04	-0.02	0.00	0.99	0.14	0.04
0.04	0.96	0.28	0.02	0.01	0.01
0.10	-0.28	0.96	0.00	0.02	-0.01
0.10	0.01	-0.02	-0.09	0.83	-0.56
0.86	-0.01	0.00	-0.12	0.55	0.83

of the density functional theory, where a nonlocal (screened Hartree-Fock-like) contribution to the total energy is singled out together with the noninteracting kinetic energy, and the rest is treated in a LDA. Such schemes retain the good accuracy of the total-energy calculations in the LDA, and improve the excitation energies as well. It is worth noting that underestimation of the hybridization tendencies inside the  $t_{1g}$  band in LDA+ $U$  and other schemes is likely to lead to a wrong energetics, and spoil the agreement of structural properties, calculated in the LDA,<sup>5</sup> with the experiment.

To summarize, we report conventional LDA calculations and rotationally invariant LDA+ $U$  calculations for antiferromagnetic FeO, both in the cubic and in a rhombohedrally distorted structure. In both cases LDA+ $U$  opens gaps, but these gaps are of completely different character in the two structures, and also different from the gaps appearing in other "corrected-LDA" schemes, which, in turn, differ by their physical nature from each other. We believe that this is a consequence of the local character of the Mott-Hubbard correction in the conventional LDA+ $U$  method, and neither straight LDA nor "corrected-LDA" methods provide a proper physical description of the gap formation. We argue that the ultimate method must take into account the nonlocal character of the Coulomb repulsion.

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